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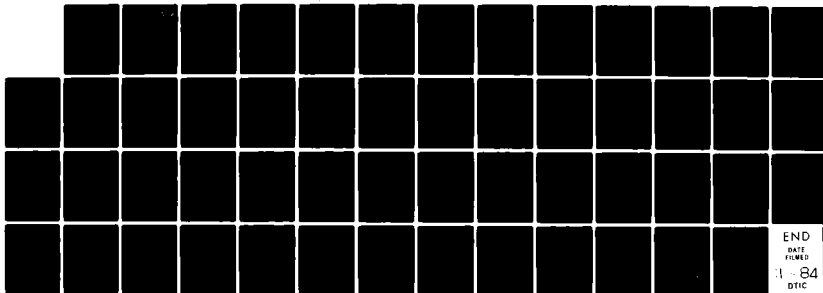
ATOMIC AND MOLECULAR GAS PHASE SPECTROMETRY(U) FLORIDA  
UNIV GAINESVILLE DEPT OF CHEMISTRY J D WINEFORDNER  
30 SEP 83 AFOSR-TR-83-1101 F49620-80-C-0005

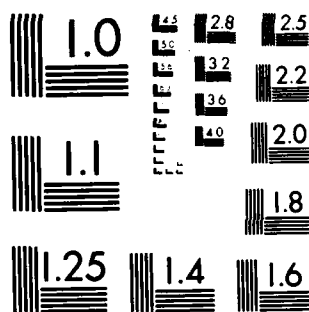
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MICROCOPY RESOLUTION TEST CHART  
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## FINAL SCIENTIFIC REPORT

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- AD-A135971
1. TITLE: Atomic and Molecular Gas Phase Spectrometry
  2. PRINCIPAL INVESTIGATOR: J.D. Winefordner  
Department of Chemistry  
University of Florida  
Gainesville, FL 32611
  3. INCLUSIVE DATES: 1 October, 1979 to 30 September, 1983
  4. CONTRACT NUMBER: F49620-80-C-0005
  5. ABSTRACT:

The major goals of this research have been to develop diagnostical spectroscopic methods for measuring spatial/temporal temperatures of combustion flames and plasmas and to develop sensitive, selective, precise, reliable, rapid spectrometric methods of trace analysis of elements present in jet engine lubricating oils, metallurgical samples, biological materials, and automobile and other engine exhausts. The diagnostical approaches have been based upon the measurement of pulsed laser excited fluorescence of seeds, such as In, Tl, Pb, etc., introduced into the flames, plasmas, or hot gases or in the case of flames, the measurement of natural flame species as OH. Because of the excellent fluorescence signal to noise ratios, it has been possible to measure temperatures of combustion flames for volumes smaller than  $1 \text{ mm}^3$  and for single laser pulses of a few nanoseconds. The technique with the most promise for use in combustion flames and in reactors is based upon thermally assisted fluorescence of an externally introduced seed as Tl or In or of an internal species as OH. By exciting the species with a dye laser and measuring the fluorescence from energy levels thermally excited from the laser excited state, the flame (plasma) temperature can be readily measured ( $\pm 10^\circ\text{C}$ ) for a volume  $< 1 \text{ mm}^3$  and for a single laser pulse.

Other diagnostical studies during the past 4 years have included: an

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evaluation of the spatial and spectral characteristics of the EIMAC (CERMAX) xenon point arc source; study of the reaction sequences and quantitative changes of alkaline earth phosphates in the presence of lanthanum salts; derivation of the rate equations describing the temporal behavior of 3-level atoms excited by a pulsed dye laser and extension of the theory to thermally assisted levels; evaluation of the significance of detection limits defined by IUPAC, measurement of the collisional redistribution of radiatively-excited levels of Na, Tl and Ga atoms in acetylene flames using pulsed laser excited fluorescence; development of an extended model for saturation in 2-level and 3-level atoms or molecules, including the temporal dependence; measurement of spatial and temporal characteristics of Na in a low pressure Ar or Ne glow discharge as studied by laser excited fluorescence; measurement of atom diffusion coefficients at high temperatures using an atomic absorption method; definition of the saturation spectral irradiance as applied to 2-level and 3-level energy systems and measurement of saturation for several atoms by laser excited fluorescence; experimental evaluation of diffracted stimulated emission as an analytical tool; measurement of volatilization characteristics of magnesium compounds in graphite furnaces and in combustion flames; measurement of the spectral noise distribution in acetylene/air, acetylene/N<sub>2</sub>O and other analytically important flames and in the inductively coupled plasma; a tutorial discussion of additive and multiplicative noises in analytical spectrometry; measurement of quantum efficiencies and lifetimes of atoms in the inductively coupled plasma; and measurement of atom spatial profiles in flames and plasmas using either laser excited atomic fluorescence or a new saturated absorption method.

All analytical studies have been directed towards improvement of detection limits, selectivity and reliability of measurement of atoms and towards

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Chief, Technical Information Division

the ultimate goal of single atom detection in real samples. The approaches used have consisted of either dye laser or conventional source excitation of atoms in flames, plasmas or furnaces and detection of atomic fluorescence. Pulsed  $N_2$ -pumped or excimer pumped dye laser excitation of atomic species in acetylene flames, graphite furnaces, and inductively coupled plasmas have led to detection limits in the pg/mL range for many elements. The dye laser approach is unfortunately sufficiently complex and expensive to negate its general analytical use but is still useful for selected analyses where other analytical techniques are not satisfactory either due to poor detection power or more likely due to poor spectral selectivity.

Other analytical studies have included: evaluation of nebulizer-burner systems for atomic spectroscopy; analysis of trace elements in jet engine lubricating oils, in orange juice, in biological materials, and in environmental samples; development of a chemiluminescence method based upon  $O_3$  oxidation of metal hydrides and of a chemiluminescence method based upon metastable  $N_2$ - the  $O_3$  oxidation process is used to measure As, Bi, Sb, Te and Se and the metastable  $N_2$  excitation is used to measure polycyclic aromatic hydrocarbons in gases in gas chromatographic effluents; development of an inductively coupled plasma (ICP) source with either an ICP or a flame atomizer and atomic fluorescence detection method - this approach is useful for single or multi-element detection and has detection limits as good as or better than conventional flame atomic absorption spectroscopy; development of a continuum source atomic absorption flame spectrometer with resonance flame detection and a molybdenum tube atomizer atomic absorption system - the latter system has been used to detect trace elements in sea water; and the speciation of metal species in agricultural, biological and environmental samples by thermal gas evolution and microwave excited emission - this approach allows the determina-

tion of the empirical formulae of compounds, such as mercury compounds in animal tissue. The above analytical approaches have been highly successful in terms of analytical figures of merit. However, the approach to single species detection with no interferences is still far from a reality.

## 6. REVIEW OF RESEARCH;

### a. Combustion Diagnostics

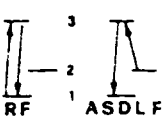
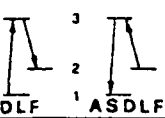
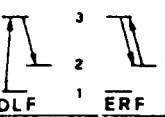
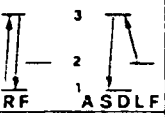
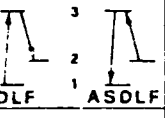

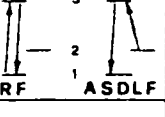
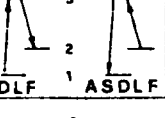
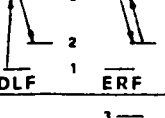
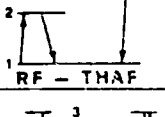
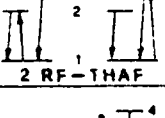
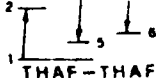
**Flame Temperature Measurements.** Combustion chemical kinetics and turbulent reacting flow studies require the development of very sensitive, selective techniques for temperature measurements with high spatial and temporal resolution. The PI's laboratory has been involved with such studies for over 20 years and especially with laser enhanced fluorescence (LEF) during the past 4 years.

There are 12 LEF approaches<sup>76</sup> which are or should be suitable for absolute temperature measurements in flames, hot gases, plasmas, etc., with good spatial ( $\leq 20$  ns) resolutions. Although the PI's laboratory has not been involved with all of these approaches, they have been involved with most of them and so a review of the 12 approaches will be performed by use of a summarizing table. All of the LEF approaches are for atomic fluorescence; however the molecular fluorescence approaches are similar to several of the atomic ones and can be derived assuming a careful choice of significant levels and the governing parameters. The table consists of 12 rows (methods) and 23 columns (characteristic parameters). The characteristics are explained as footnotes. Apart from the method name, the type of transitions involved, the corresponding temperature expression and pertinent references, all the other entries are given as questions whose answer can be "yes" (Y), "no" (N) or "depends on the specific case" (D). The entry question is formulated in such

a way that an answer "no" corresponds to a preferable quality. The principal investigator stresses the fact that one should not sum all the no's to find out the better method, because some entries can be of overwhelming importance with respect to others. For instance, a yes in column 9, corresponding to the need of knowledge of the collisional constants  $k$ 's, can preclude the applicability of the technique.

As stated previously, the methods itemized here have already been utilized experimentally and/or proposed theoretically in the literature. The overall rating (which reflects the personal bias of the principal investigator) of the methods given here and itemized on the ground of their theoretical features and/or experimental constraints, would be useful to the potential users of such techniques. The references (designated with prefix 0) refer to work by the PI but not supported by the AFOSR contract F49620-80-C-0005 (Oct. 1, 1979 - Sept. 30, 1983) and to other workers (than the PI) are listed on the supplementary reference list at the end of this section. All other references to the PI's AFOSR supported research have numbers 1-80 referring to the Reference List (Section 7).

Table I. ATOMIC LEF TECHNIQUES FOR TEMPERATURE MEASUREMENTS

METHOD NAME (1)	TYPE OF TRANSITIONS (2)	TEMPERATURE EXPRESSIONS (3)	MORE THAN ONE $\lambda_{\text{excit}}$ (4)	MORE THAN ONE $\lambda_{\text{deexc}}$ (5)	SATURATION (6)	STEADY STATE (7)	TIME RESOLUTION (8)
1 2 LINE LINEAR		$T = \frac{V_{12}/k}{\ln \frac{E_{23}}{E_{13}} + \ln \frac{A_{32}}{A_{31}} + 5 \ln \frac{\lambda_{32}}{\lambda_{31}} + \ln \frac{B_{31-13}}{B_{31-23}}}$	Y	N	N	Y	N
2 2 LINE LINEAR		$T = \frac{V_{12}/k}{\ln \frac{E_{23}}{E_{13}} + 6 \ln \frac{\lambda_{23}}{\lambda_{13}} + \ln \frac{B_{32-13}}{B_{31-23}}}$	Y	Y	N	Y	N
3 2 LINE LINEAR		$T = \frac{V_{12}/k}{\ln \frac{E_{23}}{E_{13}} + \ln \frac{A_{32}}{A_{31}} + 5 \ln \frac{\lambda_{32}}{\lambda_{31}} + \ln \frac{B_{32-23}}{B_{32-13}}}$	Y	N	N	Y	N
4 2 LINE SATURATION ST. STATE		$T = \frac{V_{12}/k}{\ln \left( \frac{C_1}{C_2} \cdot \frac{B_{31-13}}{B_{31-23}} - \frac{C_3}{C_2} \right)}$	Y	N	Y	Y	N
5 2 LINE SATURATION ST. STATE		$T = \frac{V_{12}/k}{\ln \left( \frac{C_1}{C_2} \cdot \frac{B_{32-13}}{B_{31-23}} \cdot \frac{A_{31}}{A_{32}} \cdot \frac{\lambda_{32}}{\lambda_{31}} - \frac{C_3}{C_2} \right)}$	Y	Y	Y	Y	N
6 2 LINE SATURATION ST. STATE		$T = \frac{V_{12}/k}{\ln \left( \frac{C_1}{C_2} \cdot \frac{B_{32-13}}{B_{32-23}} - \frac{C_3}{C_2} \right)}$	Y	N	Y	Y	N
7 2 LINE SATURATION PEAK		$T = \frac{V_{12}/k}{\ln \frac{g_2(g_1+g_3)}{g_1(g_2+g_3)} + \ln \frac{B_{31-13}}{B_{31-23}}}$	Y	N	Y	N	Y
8 2 LINE SATURATION PEAK		$T = \frac{V_{12}/k}{\ln \left( \frac{g_2(g_1+g_3)}{g_1(g_2+g_3)} \cdot \frac{A_{31}}{A_{32}} \cdot \frac{\lambda_{32}}{\lambda_{31}} \right) + \ln \frac{B_{32-13}}{B_{31-23}}}$	Y	Y	Y	N	Y
9 2 LINE SATURATION PEAK		$T = \frac{V_{12}/k}{\ln \frac{g_2(g_1+g_3)}{g_1(g_2+g_3)} + \ln \frac{B_{32-13}}{B_{32-23}}}$	Y	N	Y	N	Y
10 COLLISIONAL 2 LINE RATIO		$T = \frac{V_{23}/k}{\ln \frac{g_1 A_{31} \lambda_{23}}{g_2 A_{21} \lambda_{31}} + \ln C_4 + \ln \frac{B_{21-12}}{B_{11-12}}}$	N	Y	N	Y	N
11 COLLISIONAL 4 LINE RATIO		$T = \frac{V_{23}/k}{\ln \frac{g_1(A_{31} \lambda_{23})^2}{g_2(A_{21} \lambda_{31})^2} + \ln C_5 + \ln \left( \frac{B_{21-12}}{B_{11-12}} \cdot \frac{B_{21-13}}{B_{11-13}} \right)}$	Y	Y	N	Y	N
12 THERMALLY ASSISTED		$T = \frac{V_{14}/k}{\ln \frac{g_4 A_{46} \lambda_{15}}{g_1 A_{15} \lambda_{46}} + \ln C_6 + \ln \frac{B_{15-12}}{B_{46-12}}}$	N	Y	N	Y	N



COLLISIONAL CONSTANTS (9)	A's VALUES (10)	$\Delta\lambda_L \gg \Delta\lambda_a$ (11)	DETECTOR CALIBRATION (12)	$E_{\lambda}$ Laser (13)	$\Delta\lambda$ Laser (14)	$\lambda$ Laser (15)	$\Delta t$ Laser (16)	PRE-FILTER (17)	POST-FILTER (18)	SELF ABSORPTION (19)	COHERENCE LET, LEC (20)	RESONANT SCATTERING (21)	POOR S/N RATIO (22)	REFERENCES (23)	METHOD NAME (1)
N	Y	Y	N	Y	Y	Y	D	Y	D	Y	N	Y	Y	01-011	2 LINE LINEAR
N	N	Y	Y	Y	Y	Y	D	Y	Y	Y	N	N	Y	1,2,12	2 LINE LINEAR
N	Y	Y	N	Y	Y	Y	D	Y	N	Y	N	Y	Y	27,30 48	2 LINE LINEAR
Y	D	Y	N	N	N	D	D	N	D	N	D	Y	N		2 LINE SATURATION ST. STATE
Y	Y	Y	Y	N	N	D	D	N	Y	N	D	N	N	1,2,12	2 LINE SATURATION ST. STATE
Y	D	Y	N	N	N	D	D	N	N	N	D	Y	N	27,30	2 LINE SATURATION ST. STATE
N	N	N	N	N	N	D	N	N	D	N	D	Y	Y		2 LINE SATURATION PEAK
N	Y	N	Y	N	N	D	N	N	Y	N	D	N	Y	017,018	2 LINE SATURATION PEAK
N	N	N	N	N	N	D	N	N	N	N	D	Y	Y	1,2,12	2 LINE SATURATION PEAK
Y	Y	Y	Y	N	N	N	N	N	D	D	N	Y	D	27,30	2 LINE SATURATION PEAK
Y	Y	Y	Y	N	N	D	D	N	D	D	D	Y	D		2 LINE SATURATION PEAK
D	Y	N	Y	N	N	N	N	N	D	D	N	N	Y	019	COLLISIONAL 2 LINE RATIO
															COLLISIONAL 4 LINE RATIO
														1,2,12, 18,27, 43,47,48, 68,74,76	THERMALLY ASSISTED

## FOOTNOTES TO TABLE 1

### 1. Method name

Because all the techniques require the applicability of the Boltzmann relationship between the levels, a two-line ratio measurement is always required. For method 11, a further two-line ratio measurement is necessary. For method 12, a Boltzmann plot with 3 or more points corresponding to lines coming from different energy levels has to be preferred.

2 Line Linear: involves two excitation/fluorescence transitions and linear interaction between the atoms and the laser field.

2 Line Saturation Steady State: involves two excitation/fluorescence transitions and saturation. Steady state must be reached during the laser pulse.

2 Line Saturation Peak Detection: involves two excitation/fluorescence transitions and saturation. Measurements should be performed at the peak of the waveform before the atomic system relaxes to the steady-state-3-level condition.

Collisional 2 Line Ratio: involves two fluorescence transitions from the laser excited level (linear or saturated) and from a collisionally populated level.

Collisional 4 Line Ratio: involves two excitation transitions (linear or saturated) and 4 fluorescence transitions from the laser excited levels and from a collisionally populated level.

Thermally Assisted: involves detection of transitions from two levels (at least) collisionally populated from a laser excited level (linear or saturated).

## 2. Type of Transition

RF = Resonance Fluorescence

ASDLF = Anti Stokes Direct Line Fluorescence

DLF = Direct Line Fluorescence

ERF = Excited Resonance Fluorescence

THAF = Thermally Assisted Fluorescence

Methods 1 to 9 are applicable to Tl-like atoms, with excitation of the higher level 3 from the ground state 1 and from an intermediate state 2.

Methods 10, 11, and 12 are applicable to Na-like atoms exciting level 2 from the ground state 1 and detecting fluorescence signals from collisionally excited levels 3. The energy gap between levels 2 and 3 has to be of the order of the thermic energy to give an acceptable temperature precision in the measurements. Considering a more complete set of energy levels and collisional and radiative constants, Tl-like atoms can be treated with such schemes.

Methods 1 to 11 involve 3 level atoms, while method 12 involves a 4 level (or more) atom.

## 3. Temperature Expressions

All the relationships between the temperature and the measured fluorescence signal ratio, involving known or measurable parameters, are derived from the rate equation analysis of the population densities under laser excitation, where the laser spectral bandwidth is assumed to be much larger than the atomic absorption profiles (i.e., the laser is considered to act as a quasi-continuum excitation source).  $V_{ij}$  ( $\text{cm}^{-1}$ ) is the energy difference between the thermometric levels,  $k$  is the Boltzmann constant ( $k = 0.695 \text{ cm}^{-1} \text{ K}^{-1}$ ),  $A_{ik}$  ( $\text{s}^{-1}$ ) is the transition probability for spontaneous emission from level  $i$  to

level  $k$  at the wavelength  $\lambda_{ik}$  (nm),  $E_{ik}$  is the laser spectral irradiance at wavelength  $\lambda_{ik}$  expressed in  $\text{erg s}^{-1} \text{cm}^{-2} \text{nm}^{-1}$  and  $B_{ik-ge}$  is the fluorescence radiance from level  $i$  to level  $k$  after excitation from level  $g$  to level  $e$  and is expressed in  $\text{erg s}^{-1} \text{cm}^{-2} \text{sr}^{-1}$ . Use of different units for the laser spectral irradiance and the fluorescence signals can lead to a different temperature expression. The  $g$ 's are the multiplicities of the levels and  $C_1$ ,  $C_2$ ,  $C_3$ ,  $C_4$ ,  $C_5$ , and  $C_6$  are constants containing collisional ( $k_{ij}$ ) and radiative ( $A$ 's) deactivation rates.

In the methods 5, 6, and 7, the constants are:

$$C_1 = \frac{g_3 + g_1}{g_3} + \frac{A_{32} + k_{32}}{k_{21}}$$

$$C_2 = \frac{g_1}{g_2} \left( \frac{g_2}{g_3} + \frac{A_{31} + k_{31}}{k_{31}} \right)$$

$$C_3 = \frac{g_3 + g_2}{g_3}$$

In method 10,  $C_4$  is:

$$C_4 = \frac{k_{32}}{k_{32} + k_{31} + A_{31}}$$

In method 11,  $C_5$  is:

$$C_5 = \frac{k_{23} + k_{21} + A_{21}}{k_{32} + k_{31} + A_{31}} = \frac{\tau_3}{\tau_2}$$

that is just the ratio between the lifetimes of levels 3 and 2. In method 12, assuming that  $(k_{32} + A_{32}) \ll (k_{31} + A_{31})$  and  $(k_{42} + A_{42}) \ll (k_{41} + A_{41})$ ,  $C_6$  is:

$$C_6 = \frac{1 + (k_{31} + A_{31})/\Sigma_h k_{3h}}{1 + (k_{41} + A_{41})/\Sigma_h k_{4h}}$$

where h refers to all the other collisionally excited levels.  $C_6$  is practically unity in most cases.

#### 4. More than One Laser Wavelength Needed?

In the methods involving more than one laser wavelength, to achieve temporal resolution, usually one pump laser ( $N_2$ , Nd-YAG or XeCl excimer) is passed through a beamsplitter to pump simultaneously two dye lasers that, after an appropriate optical delay, are directed along the same path through the flame in opposite directions. In this way, two excitation pulses at two frequencies are available in succession (within the turbulence time scale ( $<1 \mu s$ )). True single-shot measurements are possible only with methods 10 and 12.

Concerning the best laser characteristics, a high repetition rate laser

would be generally advisable, e.g., a copper vapor pumped dye laser. Pulse duration and peak power have to be considered keeping in mind column 6, 7, 11, and 20. For best performances, the linear methods require long pulses with low peak power (flash lamp pumped dye laser). All the other methods are in general performed with short length pulses ( $\sim 10$  ns) and high peak power ( $N_2$ , Nd-YAG, excimer pumped dye lasers). Moreover, the saturation peak methods require pulses with a very fast leading edge.

#### 5. More than One Detection Wavelength Needed?

To achieve temporal resolution, methods requiring two wavelength detection are usually performed with two receiving optical systems, two monochromators and two photomultipliers. Method 12 is preferentially done with the aid of an optical multichannel analyzer to detect several lines simultaneously.

#### 6. Is Saturation Necessary?

Clearly saturation is needed for methods from 4 to 9. Saturation is also welcomed for methods 10, 11, and 12 since it will result in more intense fluorescence signals. However, in methods 1, 2, and 3 saturation must be avoided. In general, with pulsed laser excitation, a preliminary check is suggested to verify the linearity (methods 1 to 3) or the saturation conditions (methods 4 to 9).

#### 7. Is Steady State Necessary?

Except for the Saturation Peak methods, all other methods require steady state to be reached during the laser pulse. Here, there are conflicting requirements because short pulses can preclude the applicability of the steady state rate equation approach, especially in low pressure flames, but long

laser pulses enhance the possibility of laser induced effects (see column 20). In principle, for short laser pulses, high quenching (low quantum efficiency) reservoirs are better because of their shorter response time.

#### 8. Is Time Resolution Necessary?

Although this applies only to methods 7, 8, and 9, it is always advisable to have this possibility. To detect the time resolved fluorescence pulse, a very fast response photomultiplier and a sampling oscilloscope are needed.

#### 9. Is Knowledge of the Collisional Constants Necessary?

The need for collisional constants knowledge results from the final relationship used to calculate the temperature (see column 3). Collisional constants are usually unknown, and therefore no absolute T values can be obtained. One could, however, approximately evaluate the influence of these constants by measuring the fluorescence ratio in a flame of known temperature. Sometimes the deactivation rates (collisional and radiative) can be evaluate from the temporally resolved fluorescence decay.

#### 10. Is Knowledge of the gA-Values Necessary?

Methods 1, 3, 5, 8, 10, 11, and 12 obviously require knowledge of the transition probability for spontaneous emission. For methods 4, 5, and 6, the A's are in the  $C_1$  and  $C_2$  constants. Evaluation of the relative magnitude of radiative and collisional rate is necessary.

The gA values can be obtained by means of a careful evaluation of published values. It should be remembered that the gA value refers to the upper level, i.e.,  $g_u A_{u1}$  (u = upper, l = lower). When the literature gives gf values (f is the absorption oscillator strength), then gf stands for  $g_l f_{lu}$ .

The relation to use to calculate A (in  $s^{-1}$ ) from f is:

$$A_{ul} = \frac{g_l f_{lu}}{1.5 \lambda^2 g_u}$$

where  $\lambda$  is expressed in cm.

11. Is It Necessary that the Laser Spectral Bandwidth  $\Delta\lambda_l$  Be Much Greater than the Absorption Bandwidth  $\Delta\lambda_a$ ?

This is a necessary requirement for the linear methods 1, 2, and 3 and for the saturation steady-state methods 4, 5, and 6 since the relationships to be used were derived for a continuum source. Besides, with a continuum excitation source, we are sure to interact with all absorbing atoms irrespective of the type of broadening (homogeneous or inhomogeneous). However for methods 7 to 12, this requirement can be relaxed.

12. Is Calibration of the Detection System Needed?

This is clearly the case when different fluorescence  $\lambda$ 's are involved. The calibration needs to be done with a standard ribbon tungsten lamp, operated at the specified current, checking for polarization effects and second order overlapping effects. Ideally, the solid angle subtended by the monochromator to the lamp should be the same as subtended when the lamp is replaced by the flame and fluorescence is measured. When the operating current for the lamp is specified, the best bet is (probably) to use a calibrated low resistance (standard resistance) and adjust the current to the lamp while measuring (with a digital voltmeter) the voltage drop across the resistance.



13. Is Measurement of the Laser Irradiance Necessary?

This is a must for linear methods and very advisable for all methods. Several detectors should be used and intercalibrated, for example, calibrated photodiodes and joulemeters. In any case, the linearity of the detector response should be carefully checked. When using neutral density filters, one should calibrate the filters at the wavelength of interest and check the calibration if the previous one was made years before (filters age).

14. Is Measurement of the Laser Bandwidth Necessary?

The best procedure is to scan slowly the dye laser across the absorption profile while simultaneously recording the wavelength integrated fluorescence signal. This procedure requires that the system response to the applied field is linear, i.e., no saturation should be present. Therefore, the scanning should be made with a suitable neutral density filter in front of the laser beam.

15. Is Measurement of the Laser Beam Dimensions Necessary?

This is a must for the linear methods. For the other methods, requiring two wavelength excitation, a check of the relative dimensions of the probe volume illuminated by the two laser beams is necessary. The best procedure is probably to expand the laser beam to assure spatial homogeneity and limit its size with a diaphragm before the flame. Photographs can be taken and size evaluated from them.

16. Is Measurement of Pulse Duration Necessary?

This is very advisable for all the methods that need more than one laser wavelength excitation except the peak methods 7, 8, and 9. This is necessary

when a boxcar is used for the measurements; usually its gate width largely exceeds that of the laser pulse and therefore different signals will be obtained for different laser pulse durations. In methods 10 and 12, a preliminary check of the laser pulse length is suggested to assure reaching the steady state conditions.

17. Are Pre-Filter Effects Important?

Pre-filter effects occur because there are illuminated regions not viewed by the detector. Pre-filter effects are not important in the saturation methods and in the 10, 11, and 12 methods because the fluorescence signals are independent of the laser power.

18. Are Post-Filter Effects Important?

Post-filter (self-reversal) effects occur because they are nonilluminated regions viewed by the detector. Post-filter effects can be present in all the fluorescence experiments and can be minimized considering transitions to a slightly populated lower level.

19. Is Self-Absorption Important?

Self-absorption occurs within the region illuminated by the excitation source and viewed by the detector. When the system is saturated, the absorption coefficient goes to zero and self-absorption is absent.

20. Are Coherence, Laser Enhanced Ionization and Laser Enhanced Chemistry Effects Important?

Coherence occurs when the stimulated absorption rate is larger than the Rabi frequency. For a continuum excitation source ( $\Delta\lambda_l \gg \Delta\lambda_a$ ) and in flames

and plasmas at atmospheric pressure where collisions are very frequent, coherence effects can probably be safely disregarded. Laser Enhanced Ionization (LEI) and Laser Enhanced Chemistry (LEC) do indeed occur in flames. These effects are less important for short ( $\sim 10$  ns) laser pulses, but they must be taken into account, if present. One should note that, even if short pulses are welcomed for minimizing these effects, they do not always allow the system to reach steady state (see column 7). Saturation methods involving two laser line excitation can be sensitive to multiphoton ionization if wavelength resonances are present. Concerning the LEC effects, in general they modify the absolute but not the relative magnitude of the fluorescence signals and, hence, the temperature measurement should be correct.

#### 21. Is Resonant Scattering Important?

Here scattering includes also spurious reflections. One should be aware that scattering has always got to be checked when measuring resonance fluorescence.

#### 22. Is the Expected S/N Ratio Low?

Generally anti-Stokes fluorescence signals, excited resonance fluorescence signals, and thermally assisted fluorescence signals are likely to be low; because of the Boltzmann factor in the collisional constants, the metastable level and the collisionally populated levels, higher than the excited level are weakly populated at relative low temperatures. The linear methods suffer because of the low power of excitation. The 2 Line Saturation Peak methods could have low signals mainly limited by the temporal resolution needed.

23. Are References Available? (References designated OX refer to list at end of this section; all other references refer to list at end of Report; latter ones supported by this 4 year AFOSR contract).

The 2 Line Linear methods were the first to be developed for temperature measurements because they can be employed even with conventional excitation sources (lamps).<sup>01-03</sup> The two-line atomic fluorescence technique (2 Line Linear DLF-ASDLF configuration) has been extensively used to characterize post flame gas temperatures in a variety of flames.<sup>04-011</sup> Improvements in the linear methods, using a dye laser excitation has been reported for atomic seedings<sup>1,2,12,27,30,48</sup> and for molecular fluorescence.<sup>013-016</sup>

The 2 Line Saturation Steady State methods are very difficult to apply because of the need of the collisional constants involved. Simplified relationships, obtained with reasonable assumptions<sup>1,2,12,27,30</sup> have been checked performing temperature measurements in the post burnt gases of a laboratory flame. Comparison with other techniques showed possible disagreements.<sup>1,2,12,27,30</sup>

The 2 Line Saturation Peak methods have been theoretically proposed<sup>1,2,12,27,30,48,017</sup> but a feasible study pointed out the experimental difficulties inherent in these techniques. Very recently, a variation of the 2 Line Saturation Peak (DLF-ASDLF) method, involving two upper excited states (3 and 3'), has been successfully applied to the OH molecule with a balanced-cross rate model.<sup>018</sup>

The Collisional 2 Line Ratio method for atomic seedings has only been theoretically proposed, but has been proposed and applied to the vibrational energy transfer in the laser excited OH fluorescence.<sup>019</sup>

The Collisional 4 Line Ratio technique is proposed here for the first time. Practical applications are possible if temporal resolved fluorescence decay measurements allow the evaluation of the levels lifetimes and of the  $C_5$  constant.

The Thermally Assisted Fluorescence Method has been recently developed<sup>1</sup> and applied to the atomic seedings<sup>1,2,12,27,30,48</sup> and to the native OH molecule in a methane-air flame.<sup>18,39,41</sup> Recently, Elder, et al.<sup>74</sup> has measured single pulse temperatures in  $C_2H_2/O_2/Ar$  or  $N_2$  flames with Tl atoms as the seed. Temperatures were precise and accurate to  $\pm 10-20^\circ K$  when using the 276 and 292 nm line pair. The accuracy of the measurements was compared to the Na-line reversal values. The result are shown in Table 2.

**Table II. Comparison of Thermally Assisted Fluorescence  
Temperatures Obtained in "Averaged" and "Single-Shot"  
Modes for Three C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub>/Ar Flames**

<u>Flame</u>	<u>276 nm - 292 nm</u>	<u>276 nm - 323 nm</u>	<u>323 nm - 292 nm</u>
<u>2465 K ± 10 K</u>			
Averaged <sup>1</sup>	2440 K ± 50 K <sup>3</sup>	2439 K ± 45 K <sup>3</sup>	2447 K ± 100 K <sup>3</sup>
Single-Shot <sup>2</sup>	2470 K ± 11 K	2475 K ± 30 K	2456 K ± 32 K
 <u>2314 K ± 12 K</u>			
Averaged <sup>1</sup>	2308 K ± 30 K	2326 K ± 50 K	2316 K ± 130 K
Single-Shot <sup>2</sup>	2308 K ± 14 K	2301 K ± 36 K	2310 K ± 61 K
 <u>2220 K ± 14 K</u>			
Averaged <sup>1</sup>	2212 K ± 60 K	2241 K ± 72 K	3319 K ± 720 K
Single-Shot <sup>2</sup>	2225 K ± 17 K	2215 K ± 25 K	3542 K ± 313 K

- 
1. "Averaged temperatures obtained by sequentially monitoring the fluorescence over time.
  2. Temperatures given are the average of 100 separate single-shot temperature measurements.
  3. Standard deviation of the "averaged" temperature measurements determined by evaluating the standard deviation of the signal for each fluorescence signal and calculating the resulting temperature precision. The standard deviation of sixteen temperatures determined over a time period corresponding to 2400 laser shots.

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a. Spatial Profiles of Atomic Species in Flames and Plasmas

Spatial profiles of atomic and ionic species in flames and Ar-inductively coupled plasmas have been performed using LEF and a new saturated absorption method (SAM). In the LEF method, the species of concern is excited with a dye laser and the fluorescence at a  $90^\circ$  angle is measured. Since the fluorescence radiance,  $B_F$ , as well as the fluorescence signal,  $S_F$ , is proportional to the analyte number density,  $n_T$ , in all electronic states,<sup>12,27,37,54</sup> relative number density profiles can be readily carried out using the crossed laser beam-viewing optics approach. The intersection of the laser beam and the solid angle of the fluorescence collection optics involved a volume of  $<1 \text{ mm}^3$ . By movement of the laser beam, the entire spatial profile of species present in the flame, plasma, etc., is measured. By measuring a single fluorescence pulse, temporal profiles of the fluorescence as well as the number densities is also possible. Profiles of Ba,  $\text{Ba}^+$ , OH, and other atomic and molecular species have been made in flames and plasmas.<sup>29</sup> The profiles indicated the expected variation of  $n_T$  with location based upon molecular monoxide formation in flames and the channel formation in the Ar-ICP.

The SAM approach<sup>78,79</sup> involves the use of a dye laser tuned to the absorption line of concern and split into a non-saturating probe beam and a saturating pump beam, the latter being at right angles to the former. The probe beam is used to measure the total absorption along the "line-of-sight" within the absorber medium. The pump beam optically saturates a small segment of the absorption path causing the transmitted beam to increase in intensity. If the segment,  $\Delta l$ , which is saturated, is small compared to the total optical path length,  $l$ , then the relative population density,  $\Delta n/n$ , i.e., the ratio of the absorber number in the path length  $\Delta l$  to the total number in the path length  $l$  (for the cross-sectional area of the probe beam).



$$\frac{\Delta n}{n} = 1 - \left(\frac{A_S}{A_T}\right) \left(\frac{1}{1 - \frac{\Delta \lambda}{\lambda}}\right) \sim \frac{A_S}{A_T}$$

where  $A_T$  = absorbance of analyte without saturating beam and  $A_S$  = absorbance of analyte with saturating beam. If  $A_S$  and  $A_T$  are substituted for in terms of  $I_0$  the intensity transmitted by blank with saturating beam off,  $I$  the intensity transmitted by analyte with the saturating beam off, and  $I_S$  the intensity transmitted by analyte with the saturating beam on,

$$\frac{\Delta n}{n} \sim \log(I_S/I) / \log I_0/I$$

Finally, if the fluorescence signal  $F$  and the thermally emission signal  $E$  are significantly, then

$$\frac{\Delta n}{n} \sim \frac{\log[I_S - (F+E)] / [I - (F+E)]}{\log(I_0 - E) / (I - E)}$$

By using an excimer pumped dye laser, an  $C_2H_2$ -Air flame or an Ar-ICP, and Sr as the analyte, profiles such as shown in Figure 1 and Figure 2, respectively, were obtained.

### 3. Other Diagnostical Studies

The spatial and temporal characteristics of a glow discharge<sup>58</sup> has been evaluated using LEF. CW laser excitation was used to evaluate the spatial distribution of Na atoms which were sputtered from the cathode; the diffusion coefficient of Na in Ar was obtained by using time resolved measurements. From the population ratios of the emission lines from various excited levels of Na, a "milky way" plot of normalized intensity vs upper state

Figure 1: Lateral Spatial Mapping of  $\Delta n/n$  for Sr(I) at Heights of 3 (O), 5  
( ), and 8 ( $\Delta$ ) mm in an  $C_2H_2$ /Air Flame.<sup>78</sup>

Figure 2: Lateral Spatial Profiles of Sr(I) at Different Heights Above the Load Coil of 500 W ICP with an Extended Slieve Torch and The High Flow Rate Neublizer In Pencil Plasma Configuration (propane present with Ar).

excitation energy was obtained indicating a lack of thermodynamic equilibrium in such a system. A temporal and spatial region was found where the signal-to-noise ratio, S/N was optimized. The spatial region with the greatest S/N for LEF was in the Faraday dark space. Both atomic and ionic lines were detected.

A variety of studies aimed at diagnosing the excitation mechanism of the Ar-ICP have been performed.<sup>60</sup> Excitation temperatures, electron number densities, Ar metastable number densities and number densities of Ca and  $\text{Ca}^+$  analyte species were measured as a function of observation height coolant and plasma gas flow rates, nebulizer gas flow rate, and input power. These studies, although not definitive, did show that the ICP in the analytical region is close but not in LTE. Spatial number density and temperature profiles of  $\text{Ar}^*$ , Ca, and  $\text{Ca}^+$  were measured; the  $\text{Ca}^+$  spatial profiles were wider than the Ca atom profiles. The electron number densities were in the range of  $5 \times 10^{14}$  to  $1 \times 10^{16} \text{ cm}^{-3}$ . The high collision rate in the ICP resulted in nearly identical excitation and gas temperatures for Ar. These studies were consistent with a Penning ionization model.

Other diagnostical studies with the ICP included: (1) measurement of analyte atomic lifetimes and quantum efficiencies; these studies showed that the Ar-plasma was highly non-quenching and an ideal cell for atomic fluorescence;<sup>62,72</sup> (2) measurement of analytical calibration curves for ICP excited flames atomic/fluorescence spectrometry<sup>14,25</sup> and for ICP-excited ICP fluorescence spectrometry;<sup>71</sup> these studies indicated the high intensity, lack of self-reversal, and narrowness of the lines of an ICP as a source of excitation for atomic fluorescence spectrometry; (3) measurement of atomic vapor diffusion coefficients by high temperature gas chromatography with atomic absorption detection;<sup>51</sup> (4) measurement of reaction sequences and quantitative

changes as solute particles undergo vaporization of flames;<sup>40</sup> this approach involved addition of a solution of the metal species, M, of concern and of an anion, X, to a solution containing one or two different metal ions  $E_1$  and  $E_2$  and monitoring of the atomic absorption of M; information about the reaction processes were deduced from the shapes of the titration curves; (5) measurement of the vaporization sequences of magnesium compounds in a graphite furnace by detection of the resulting vapors with atomic absorption spectrometry and a second graphite furnace of a flame;<sup>63</sup> the vaporization of  $MgCl_2$  in the presence of aluminum and aluminum-calcium salts and an Ar or an Ar +  $CCl_4$  atmosphere was studied in detail; these observations were used to explain and to predict interferences for Mg in graphite furnace atomic absorption spectroscopy.

#### 4. Signal to Noise Studies

Several reviews<sup>13,57</sup> concerning noise sources, signal-to-noise ratios, and detection limits in analytical spectrometry were prepared. The shot and flicker noise sources in atomic absorption, atomic emission, and atomic fluorescence spectrometry were discussed, expressions were given, and numerical estimates were made; similarly signal expressions were given for the 3 analytical atomic methods. By means of the signal-to-noise expressions, estimates of detection limits, in atoms/cm<sup>3</sup>, were made for the 3 methods. For the case of atomic fluorescence, amplitude, wavelength, and sample modulation as well as pulsed sources and gated detectors were especially considered. The expressions presented along with ones for laser induced ionization flame spectrometry and laser induced flame photoacoustic spectrometry allow one to compare the various atomic methods under ideal conditions as well as real, but less ideal, conditions. It is possible by means of laser excited atomic

fluorescence spectrometry to detect one atom/cm<sup>3</sup> of hot gases. This sort of detection power is not available in any of the other atomic methods, except possible laser induced resonance ionization spectrometry in furnaces.

Fujiwara, et al<sup>10</sup> evaluated the spectral noise flame background distribution of several analytical flames, including C<sub>2</sub>H<sub>2</sub>/air, C<sub>2</sub>H<sub>2</sub>/N<sub>2</sub>O, propane/N<sub>2</sub>O, H<sub>2</sub>/air, and on iso-octane liquid fuel flame. The noise sources were evaluated by means of counting statistics. When using a dc detection system, irradiation of any flame by a continuum source increased both shot and flicker noises. When a modulated source and a lock-in detection system are used, flicker noise due to flame background emission is significantly reduced. Therefore, for a typical analytical system where ac detection is used, flame background shot noise is dominant, not flame background flicker noise. However, with an external source illuminating a flame, source scatter and source induced molecular fluorescence shot and flicker noises can become dominant.

The nature of flame background noise in emission (flame emission) and in continuum excited fluorescence (flame emission, molecular fluorescence, and scatter) can be summarized as follows:

(i) flame background emission flicker noise is primarily a result of flame gas species, as OH, C<sub>2</sub>, CH, CN, HPO, etc;

(ii) flame background emission flicker noise is more significant than source induced fluorescence and scatter flicker noises in almost all flames and spectral regions, with the major exception being the non-specific scatter and molecular fluorescence flicker noise existing in short (~230 nm) wavelengths;

(iii) lower temperature flames (air supported) are less noisy than higher temperature flames and are usually shot noise limited; higher temperature flames (N<sub>2</sub>O supported) are usually flicker noise limited in either emission measurements or in fluorescence measurements;

(iv) the iso-octane liquid fuel acetylene/air flame is generally much less noisy than the  $C_2H_2/N_2O$  and  $C_3H_8/N_2O$  flames but somewhat noisier than the  $C_2H_2$ /air and  $H_2$ /air flames;

(v) fuel rich conditions result in lower total noise and in lower shot and flicker noises than fuel-lean or stoichiometric conditions;

(vi) the experimental system contributes negligibly to the total noise, the total shot noise and the total flicker noise. Finally, amplitude, wavelength, or sample modulation in atomic fluorescence spectrometry (AFS) will discriminate against flame emission background flicker noise. Amplitude modulation in AFS will not discriminate against source scatter or source induced molecular fluorescence flicker noise whereas wavelength and sample modulation will discriminate against continuum (broad band) scatter, emission, and background fluorescence. Amplitude modulation in atomic emission spectrometry will not discriminate against flame emission background flicker noise. However, as before, wavelength or sample modulation will discriminate against broad band emission flicker noise.

Noise power spectra for the ICP were determined under various conditions, by Fast Fourier Transform (FTT) digital techniques.<sup>33</sup> The major noise types observed were white noise, low frequency noise, and high frequency proportional noise. The high frequency proportional noise increased with concentration of analyte and radio frequency input power. The high frequency proportional noise decreased with increasing nebulizer flow rate and coolant gas flow rate. The low frequency noise components extended to higher frequencies as the resonance wavelengths of the measured transitions increased. Changing the observation height in the plasma determined which noise types were present in the noise power spectrum. At observation heights near the power coils, all three noises types were present, whereas, low frequency noise predominated at

significantly greater heights. Changing the torch design changed the relative amplitudes of the different high frequency proportional noise components but did not greatly change their respective peak frequencies. In Table 3, the effect of changing certain ICP parameters relative to base conditions are given.

The multielement atomic fluorescence-emission spectrometric system (continuum source of excitation) has been evaluated for individual noise contributions as a function of flame type, modulation approach, and atom type.<sup>46</sup> The flames studied included Ar-shielded air/acetylene, Ar-shielded N<sub>2</sub>O/acetylene, Ar-shielded N<sub>2</sub>O/propane, and an air/acetylene flame with a liquid fuel component (isooctane and jet engine oil). The modulation methods included AM (amplitude modulation) and WM (wavelengths modulation) as well as CW (continuous wave excitation with DC detection). The elements and wavelengths studied include (228.2 nm), Mg (285.2 nm), Cu (324.7 nm), Ca (422.7 nm), and Na (589.0 nm); Bi (306.8 nm) was studied in the air/acetylene flame only. Useful conclusions were: the N<sub>2</sub>O/propane flame was less useful than the two acetylene-based flames; AM is superior for transitions with wavelengths <350 nm and WM for ones >350 nm; analyte emission/fluorescence flicker noise becomes significant for analyte concentrations above ~100X the limiting detectable concentration; the air/acetylene flame should always be used instead of the N<sub>2</sub>O/acetylene flame unless atomization is insufficient to obtain reasonable signal levels; the acetylene/air-isooctane flame has noise characteristics similar to the acetylene/air flame and has definite analytical possibilities, particularly for the analysis of jet engine lubricating oils for trace wear metals; and atomic fluorescence spectrometry gives the best results with



Table 3. Summary of General Trends in Noise Components  
with Change in Operational Parameters

<u>Change Mode</u>	<u>Change In d.c. Signal</u>	<u>White Noise Amplitude</u>	<u>Change Observed In Proportional Noise Amplitude</u>	<u>Low Frequency</u>	
				<u>Amplitude</u>	<u>10% Point</u>
Increased analyte concentration	+*	+	+	+	- <sup>†</sup>
Increased coolant gas flow rate on analyte or background emission	-	-	-	0 <sup>‡</sup>	-
Increased wavelength of emission of background <sup>§</sup>	NA	-	0	0	+
Increased observation height (with Y emission only)	NA	+	-	+	+
Increase RF power on analyte emission	+	+	+	+	0
Increased nebulizer flow rate on analyte	-	0	-	-	+
Different torch design	0	0	+	-	-

\* Increase.

† Decrease.

‡ Remains approximately the same.

§ An exception occurred for emission background yttrium monoxide condition.

|| Not applicable.

\*\* Proportional noise peaks were at ~200 Hz and at ~2800 Hz.

the isooctane flame.

The statistical measuring limit of detection has been examined by three different approaches including the IUPAC definition.<sup>70</sup> The other two approaches include a graphical one and a propagation of errors one. The propagation of errors approach is shown to be considerably more conservative and safer to use since the influence of slopes and intercept errors in the calibration curve are considered as well as random errors in the blank. The three approaches are applied to the same data set and the limitations of the graphical and IUPAC approaches are noted. Other limit of detection approaches were also mentioned.

#### 5. Other Fundamental Studies

The saturation spectral irradiance<sup>6,49,59</sup> parameter is defined for a spectrally continuum laser source interacting in a non-linear manner with a dilute atomic or molecular vapor. However, this important parameter is meaningful only when steady state conditions are present. For short excitation pulses, even though steady state is attainable, when the optical transition is saturated, the saturation parameter can not be evaluated from the fluorescence saturation curve  $B_F$  vs  $E_v$ . Therefore, such a definition of  $E_v^s$  loses its meaning even for a simple 2-level system, and so serious experimental errors in its determination can result. The same conclusions apply to 3-level and more-level systems. Methods of evaluating accurately  $E_v^s$  are discussed by Omenetto et al. Also  $E_v^s$  for a 3-level system (Na and Tl) is compared to  $E_v^s$  for a 2 level case. It is shown that  $E_{v13}^{s-3L}/E_{v13}^{s-2L}$  for Na-like atoms is within 10% of unity as long as the coupling rates between states 3 and 2 are much greater than between states 3 and 1 and 2 and 1. For Tl, however, state 2 is a metastable level and acts as a sink and so

$$\frac{E_{v13}^{s-3L}}{E_{v13}^{s-2L}} \approx 2 \left( \frac{g_1 + g_3}{g_1} \right) \left( \frac{k_{21}}{A_{3L} + k_{32}} \right)$$

where the g's are statistical weights, the A is the spontaneous emission transition rate and the k's are non-radiational rate constants between the levels shown. Since the final term in parenthesis is much less than unity (say 0.01),  $E_{v13}^{s-3L} \ll E_{v13}^{s-2L}$ .

The influence of gate width, laser pulse length, and lifetime of the fluorescence species upon the temporal and time integrated fluorescence signal level for a hypothetical 2-level system has been shown to be critical.<sup>49</sup> It is shown that even in the relatively simple case of a fully saturating, rectangular laser pulse, the integrated signal is still dependent upon radiative and collisional rate constants. On the other hand, this dependency can be used to measure these rate constants. The only case where the integrated signal becomes independent of these rate constants is the case of a perfectly rectangular portion being sliced out of the time dependent fluorescence signal.

The ratio of the fluorescence intensities from the two lines of the yellow sodium doublet has been investigated<sup>15</sup> in several hydrogen-based and acetylene-based flames and with various types of lasers as excitation sources. The systematic deviation from 2 for the ratio  $D_2/D_1$  when either  $D_1$  or  $D_2$  are used as exciting transitions can be simply explained by the relative difference in the values of the collisional mixing constants between the excited P-levels and the collisional quenching constants transferring atoms from both P-levels to the ground S-level. Results obtained in flames characterized by

different values of quantum efficiency follow the behavior predicted by the fluorescence expressions obtained by a simple, steady-state theoretical approach.

The broadening of the absorption profile in hydrogen-based flames diluted with argon and nitrogen is discussed theoretically and demonstrated experimentally with a pulsed tunable dye laser.<sup>31,34</sup> This broadening is evaluated from the half-width of the profile obtained by scanning the laser beam through the atoms in the flame while monitoring the resulting fluorescence with a high luminosity monochromator, i.e., by observing a fluorescence excitation profile. Results are given for the elements Ca, Sr, Na, and In. It is shown that the halfwidth of the atomic profile depends approximately upon the square root of the log of the laser irradiance. This dependence stems from a theoretical treatment based upon the interaction of a gaussian laser profile and a gaussian atomic profile. It is also shown that if the laser spectral bandwidth exceeds by ~5-10 times the absorption halfwidth, the fluorescence excitation profile provides a simple means for a reliable evaluation of the laser bandwidth.

Laser induced fluorescence background of several flame species including  $C_2$ , CH, CN, OH, was investigated<sup>18,21</sup> for  $C_2H_2$ /air and  $C_2H_2/N_2O$  (and also in kerosene-air and gasoline-air flames) using a  $N_2$  laser-dye laser system. In all cases, the resulting fluorescence spectra extend over a broad wavelength range contributing to background noise in atomic fluorescence spectrometry. In the liquid fuel flames, fluorescence of polyaromatic molecules was observed. In addition, molecular emission spectra in the RF excited-Ar-ICP were obtained<sup>28</sup> for OH, NO, and NH as well as stable monoxides of rare earths at low and high observation heights. These spectral features contribute to background emission noise in ICP-atomic emission spectrometry assuming mea-

measurements are made at low or high observation heights. If measurements are made at conventional observation heights 15-25 mm above the top of the load coil, monoxide emission is no problem.

The Eimac xenon arc lamp with integral parabolic reflector was evaluated as a source of excitation in analytical spectrometry.<sup>44</sup> The proper lens system for transferring radiation from the source to a cell is discussed with data showing an experimentally optimized (trial and error) arrangement of 3 lenses. Lamp ventilation is considered with regard to stability and lamp lifetime. Difficulties with starting the Eimac lamp in the same room as a minicomputer are considered. The construction and operation of a computer-controlled radiometer is described. The radiometer is used to measure the spatial distribution (y,z) of relative intensities (x) of the Eimac lamp by means of three dimensional projection and contour plots. Plots are given for three wavelengths (213.9 nm, 328.1 nm, and 589.6 nm) and for three lamp currents (11A, 12A, and 13A) at one wavelength (589.6 nm).

#### b. Analytical Spectrometric Studies

##### (1) Laser Excited Atomic Spectrometry

Winefordner et al,<sup>27,38,50,54</sup> have reviewed the analytical capability of laser excited atomic fluorescence.

Both a frequency-doubled flashlamp dye laser and a N<sub>2</sub> laser-dye laser have been used to excite atoms in flames. Epstein et al.<sup>22,23</sup> has reported detection limits for Fe, Ni, and Sn of 0.06 ng/mL, 0.5 ng/mL, and 2 ng/mL, respectively, by laser excited atomic fluorescence spectrometry, LEAFS. Multi-pass excitation and frequency narrowing gave considerable improvements of detection limits (>10X); the above detection limit values contained those improvements. LEAFS was applied to the direct determination iron in NBS-

simulated fresh water, NBS-unalloyed copper, and NBS-fly ash. LEAFS was also applied to the determination of Ni and Sn in NBS-river water, NBS-unalloyed copper, and NBS-fly ash. Spectral interferences were found in all cases to be negligible as compared to atomic emission methods based on using the ICP.

A variety of analytical studies involving pulsed and cw dye laser excitation of atoms or ions in an Ar-ICP have been carried out. Currently, cw dye laser excitation<sup>8</sup> results in much poorer ( $\sim 10^2\times$ ) detection limits and has considerably less wavelength flexibility than pulsed dye laser excitation. At the current state of the art of cw dye laser systems, the consensus is that they are of little analytical use in LEAFS.

Pulsed dye laser excited fluorescence of atoms and ions in the ICP has proven to be a viable analytical approach to elemental measurements where spectral selectivity in ICP-AES is poor and/or detection power is insufficient. Epstein et al.<sup>26</sup>, Uchida et al.<sup>61</sup> and Kosinski et al.<sup>66</sup> have all been involved with the development of laser excited ICP fluorescence spectrometry as an analytical technique. The detection limits have generally been good but not as great as one would expect. Since these works, Omenetto in Ispra has used pulsed  $N_2$ -laser dye laser excitation of atoms/ion in the ICP (at the conventional emission observation height of 20 mm above the load coil) and has obtained detection limits of  $\sim 0.5$ -5 ng/mL for many of the refractory like elements. Our results at higher observation heights and with the long torch (emission background and noise is much less at high observation heights but the extent of atomization and ionization is much less also) have resulted in excellent detection limits for non-refractory elements (those that are determined by AAS with an  $C_2H_2$ /air flame) but poor detection limits for the refractory elements (those that are determined by AAS with an  $C_2H_2/N_2$  flame). Detection limits for several elements by LEAFS are given in Table 5. Conclusions reached by Omenetto are summarized in Table 6.

TABLE 5  
LIMITS OF DETECTION (LOD), IN ng/mL, AS OBTAINED BY ICP EMISSION  
AND FLUORESCENCE SPECTROMETRY EXCITED BY TUNABLE DYE LASERS AND  
PULSED HOLLOW CATHODE LAMPS

Element	DL-AFS-ICP (Omenetto et al.) <sup>a</sup>		LOD ICP-AES (Boumans) <sup>6</sup>	LOD DL-ICP-AFS (JDW et al. (short))	LOD DL-ICP-AES (JDW et al. (short))	LOD HCL-ICP-AFS <sup>c</sup>	LOD DL-ICP-AES (JDW et al. (long))
	λ exc.	λ fluor.					
Al (I)	394.4	396.1	0.4	22.		30.(RF)	7.5
B (I)	249.7	249.8	4.	4.			
Ba (II)	455.4	614.2	0.7	1.	60.(RF)	75.(RF)	1.5(RF)
Ga (I)	287.4	294.4 294.3	1.	66.			6.
Mo (I)	313.3	317.0	5.	7.	4,500.(RF)	45.(RF)	150(RF)
Pb (I)	283.3	405.8	1.	42.	9,000.(RF)	37.(RF)	150
Sr (I)	288.2	251.4 251.6 251.9	1.	12.		(300)(RF)	
Sn (I)	300.9	317.5	3.	25.	500.	90.(RF)	
Ti (II)	307.8	316.2 316.8	1.	4.		(225)(RF)	
Tl (I)	276.8	352.7	7.	40.	12,000.(RF)	10.(RF)	12(RF)
V (II)	268.8	290.9	3.	4.	1,050.	600.(RF)	
Y (II)	508.7	371.0	0.6	3.	45.		105
Zr (II)	310.6	257.0	3.	7.			9,000

<sup>a</sup>Unpublished results, Ispra, Italy.

<sup>b</sup>W.J.M. Boumans and M. Bosveld, *Spectrochim. Acta*, 34B 59(1979).

<sup>c</sup>D. Demers, Baird Corp., Bedford, MA.

TABLE 6

CONCLUSIONS OF OMENETTO CONCERNING ICP-LEAFS

1. Limits of detection were superior to all previous AFS studies to all ICP-AES studies.
2. Non-resonance fluorescence was used in all cases, and thus scatter was not a problem.
3. Transitions chosen gave best detection power but other combinations were similarly suitable.
4. Optical saturation occurred in virtually all cases (laser beam diameter of 1 cm; Lambda Physik excimer pumped dye laser system).
5. The short IPC torch was used and the plasma was viewed in the same region as the ICP-AES. Thus both AES and AFS can be efficiently used.
6. The limiting noise was due to ICP background shot noise.



The major noise source in LEAFS are RF interference noise (Long and Winefordner have discussed means of greatly reducing this noise) and ICP background emission noise. At high analyte concentrations, the major noise source becomes AFS flicker due to pulse-to-pulse intensity variation. These same noise sources are also present in flame-LEAFS.

Vertical and horizontal distributions of atomic and ionic fluorescence signals<sup>61,66</sup> in ICP-LEAFS have shown the importance of optimizing the observation height and the radial position for measurements. The effect of carrier gas flow rate and interfering species upon the fluorescence signals and signal-to-noise ratios have also been studied for several analytes.

Pulsed dye laser excitation of atoms produced with a graphite filament atomizer<sup>75</sup> resulted in detection limits of 20, 3, and 5 pg for Na, Mn, and Sn, respectively. Considerable improvement of detection limits would result with use of non-resonance transitions for excitation and emission and with an improved cell design to minimize losses.

## (2) Non-laser ICP Spectrometry

The ICP is not only an excellent atomizer, ionizer, and exciter but also is an excellent source for atomic fluorescence of atoms in flames and furnaces<sup>14,20,25</sup> and of atoms and ions in a second ICP.<sup>71</sup> Epstein et al. showed that if a high concentration of some species (e.g., 10,000 µg/mL of a metal, M, solution) is introduced into an ICP, the emitted radiation is intense and the spectral shape is narrow and non-self reversed. As a result, the ICP is an excellent source of excitation for species in flames, furnaces, and ICPs. If the sample is introduced into the flame, furnace, or second ICP and a high concentration of the element of interest is introduced into the first (source) ICP, then atomic fluorescence can be detected and used to determine low con-

centrations of analytes; this method is called ICP-ICP-AFS. If the sample is introduced into the first (source) ICP, then atomic fluorescence can again be detected if a low concentration or amount of standard analyte is introduced into the flame, furnace or second ICP cell; this method is called ICP-ICP-RM where RM designates Resonance Monochromator. ICP-ICP-AFS has a much higher detection power but a poor spectral selectivity than ICP-ICP-RM. Detection limits for the three approaches are given in Table 7. The detection limits for ICP-ICP-AFS have recently been considerably improved in the PI's laboratory; these results will be given in the next annual report. In all of these cases, analytical calibration curves were linear over  $10^4$ - $10^6$  fold ranges.

By means of ICP-flame-AFS, several unique ways exist to correct for matrix scatter in flames.<sup>25</sup> In one approach, self absorption in the ICP is used, i.e., as the concentration of analyte in the ICP source is increased, self absorption occurs resulting in no further increase in fluorescence but in a linear change in the scatter signal. In the other approach, the sample is introduced into the ICP source and a low concentration standard is introduced into the flame cell. The flame cell now acts as a resonance monochromator with a narrow spectral bandpass. Since the sample is in the ICP source, scatter is much less severe. Also the flame noise is much less.

### (3) Nebulizer-Spray Chamber Studies

Ten different commercial atomic absorption nebulizer-chamber systems with a capillary burner and three laboratory-constructed ultrasonic nebulizer chamber systems with a miniflame burner were compared with respect to solution uptake rates, concentrational and absolute detection limits, efficiencies of nebulization, and common flame spectrometric interferences.<sup>45</sup> Measurements of

**TABLE 7**  
**DETECTION LIMITS (ng/mL) FOR SEVERAL ELEMENTS IN**  
**FLAMES VIA ICP-FLAME-AFS, ICP-FLAME-RM, AND ICP-ICP-AFS**

<u>Element <math>\lambda</math>(nm)</u>	<u>ICP-Flame<sup>a,c</sup>-AFS</u>	<u>ICP-Flame<sup>b,c</sup>-RM</u>	<u>ICP<sup>c</sup>-ICP-AFS</u>
Ag (328.1)	3.	2,000.	---
Ca (422.7)	4.	1,000.	2.
Cd (228.8)	0.7	700.	---
Co (240.7)	11.	5,000.	40.
Cr (357.9)	2.	7,000.	900.
Cu (324.7)	2.	2,000.	30.
Fe (248.3)	6.	6,000.	100.
Mg (285.2)	0.09	400.	---
Mn (279.5)	2.	900.	9.
Ni (232.0)	50.	3,000.	100.
Pd (363.4)	4000.	15,000.	---
Zn (213.9)	0.5	700.	6.

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<sup>a</sup>N<sub>2</sub>-separated C<sub>2</sub>H<sub>2</sub>/air flame

<sup>b</sup>H<sub>2</sub> + Air flame

<sup>c</sup>10,000  $\mu$ g/mL analyte in source ICP

both flame atomic emission (Sr, Ca, K, Na) and flame atomic fluorescence (Mg, Cu, Pb) were performed for all cases. The ultrasonic and pneumatic nebulizer systems resulted in about the same concentrational detection limits, but the former resulted in  $\sim 10^2 \times$  lower absolute detection limits. The batch type ultrasonic nebulizer gave much higher nebulization efficiencies than the continuous flow ultrasonic nebulizer or any of the pneumatic nebulizer systems. Chemical interferences were approximately the same in all nebulizer-burner systems. Nebulizer chambers with a J-bead resulted in lower detection limits than the same systems without J-beads. The ultrasonic nebulizer and a specially designed miniflame shielded burner was used in a pulsed  $N_2$  laser-dye laser AFS system.<sup>80</sup> Detection limits obtained with this system were improved over previous AFS systems as well as over most other atomic spectrometric detection limits. Detection limits for Ca, Sr, Mg, and Pb were 0.01, 0.1, 0.002, and 0.2 ng/mL, respectively.

#### (4) Speciation Studies

Evolved gas analysis-microwave emission detection is a means of determining the empirical formulae of molecular species.<sup>73,77</sup> Evolved gas analysis involved slowly vaporizing a sample as a function of temperature. The resulting molecular species are transferred to an unique single electrode 500 W microwave plasma. The microwave assembly consists of a Pt coated electrode which terminates a microwave waveguide. The microwave detection is extremely sensitive for both metals and non-metals, such as C, H, O, N, S, etc. This approach has been used to determine molecular species as mercury and arsenic compounds in plant and biological materials, sulfur in oils, impurities in rare earth compounds, Pb in air, etc.

(5) Furnace Studies

High temperature gas chromatography was used to separate inorganic species and atomic absorption was used to detect the metal constituents.<sup>51,55,65</sup> Copper in sea water was measured by this approach. It was possible to separate the matrix interference from the analyte.

(6) Chemiluminescence

Gas phase chemiluminescence of As and Sb in flames and excited by ozone has been evaluated as an analytical measurement approach.<sup>9</sup> By these approaches parts per billion concentrations of As and Sb can be measured by using flames and nanograms of As, Sb, Sn, and Se can be detected by ozone induced chemiluminescence. Both devices are suitable for use in gas chromatographic detectors. Metal hydrides of As, Sb, Sn, and Se were separated by either differential volatilization from a liquid nitrogen trap or chromatographically and detected by the ozone chemiluminescence detector system.

These latter workers used a continuous flow graphite tube furnace instead of the flame for the detection cell. The system gave results similar to conventional flame AAS but the cw furnace continually needed adjustment and occasionally needed replacement.

Diffraction stimulated emission was evaluated as an analytical method in flames and was found to fail.<sup>64</sup>

(7) Other Analytical Studies

A computer controlled multi-element atomic emission/atomic fluorescence spectrometer has been evaluated for wear metal analysis in jet engine lubricating oils,<sup>4,5</sup> orange juice,<sup>3,19,35,37</sup> and other materials.<sup>5</sup> Trace wear metals were also determined using a wavelength modulated, continuum source excited AFS system with electrothermal atomization.<sup>42</sup>

Precision of analytical measurements in AAS and linearity of analytical calibration curves in AAS is influenced by rotation of the burner head; rotation of the burner head affects the absorption path length.<sup>17</sup>

A general approach to selectivity as an analytical figure of merit was given by Fujiwara et al.<sup>23</sup> These workers have defined a selectivity index which can be used to indicate the spectral and matrix selectivity of the method. The selectivity index was used to evaluate hypothetical sea water and blood serum samples for several metals.

A versatile, high resolution, continuum source atomic absorption spectrometer with a resonance atomic fluorescence flame detector has been evaluated.<sup>62</sup> An EIMAC xenon arc source was used for all analytes. The detector consisted of a flame with a monochromator-detector at right angles to the optical axis. A second flame (the absorption cell) was placed between the source and the detection flame. To change to a different element, it was only necessary to introduce a concentration of 1-100  $\mu\text{g/mL}$  of the new element into the "detection" flame and adjust the wavelength of the large aperture monochromator to the absorption wavelength. The effective spectral bandpass of this system was determined by the absorption line widths of the absorber in the detection flame. Detection limits of 0.07, 0.12, 0.5, and 0.5  $\mu\text{g/mL}$  were obtained for Mn, Cu, Sr, and Cr, respectively. These values compared well with other atomic absorption methods. A similar continuum source resonance detector system for AAS was developed by Bower et al.<sup>11</sup>

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The major goals of this research have been to develop diagnostical spectroscopic methods for measuring spatial/temporal temperatures of combustion flames and plasmas and to develop sensitive, selective, precise, reliable, rapid spectrometric methods of trace analysis of elements present in jet engine lubricating oils, metallurgical samples, biological materials, and automobile and other engine exhausts. The diagnostical approaches have been based upon the measurement of pulsed laser excited fluorescence of seeds, such as In, Tl, Pb, etc., introduced into the flames, plasmas, or hot gases or in the case of			

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flames, the measurement of natural flames species as OH. Because of the excellent fluorescence signal to noise ratios, it has been possible to measure temperatures of combustion flames for volumes smaller than  $1 \text{ mm}^3$  and for single laser pulses of a few nanoseconds. The technique with the most promise for use in combustion flames and in reactors is based upon thermally assisted fluorescence of an externally introduced seed as Tl or In or of an internal species as OH. By exciting the species with a dye laser and measuring the fluorescence from energy levels thermally excited from the laser excited state, the flame (plasma) temperature can be readily measured ( $\pm 10^\circ\text{C}$ ) from a volume  $< 1 \text{ mm}^3$  and for a single laser pulse.

Other diagnostic studies during the past 4 years have included: an evaluation of the spatial and spectral characteristics of the EIMAC (CERMAX) xenon point arc source; study of the reaction sequences and quantitative changes of alkaline earth phosphates in the presence of lanthanum salts; derivation of the rate equations describing the temporal behavior of 3-level atoms excited by a pulsed dye laser and extension of the theory to thermally assisted levels; evaluation of the significance of detection limits defined by IUPAC, measurement of the collisional redistribution of radiatively-excited levels of Na, Tl and Ga atoms in acetylene flames using pulsed laser excited fluorescence; development of an extended model for saturation in 2-level and 3-level atoms or molecules, including the temporal dependence; measurement of spatial and temporal characteristics of Na in a low pressure Ar or Ne glow discharge as studied by laser excited fluorescence; measurement of atom diffusion coefficients at high temperatures using an atomic absorption method; definition of the saturation spectral irradiance as applied to 2-level and 3-level energy systems and measurement of saturation for several atoms by laser excited fluorescence; experimental evaluation of diffracted stimulated emission as an analytical tool; measurement of volatilization characteristics of magnesium compounds in graphite furnaces and in combustion flames; measurement of the spectral noise distribution in acetylene/air, acetylene/ $\text{N}_2\text{O}$  and other analytically important flames and in the inductively coupled plasma; a tutorial discussion of additive and multiplicative noises in analytical spectrometry; measurement of quantum efficiencies and lifetimes of atoms in the inductively coupled plasma; and measurement of atom spatial profiles in flames and plasmas using either laser excited atomic fluorescence or a new saturated absorption method.

All analytical studies have been directed towards improvement of detection limits, selectivity and reliability of measurement of atoms and towards the ultimate goal of single atom detection in real samples. The approaches used have consisted of either dye laser or conventional source excitation of atoms in flames, plasmas or furnaces and detection of atomic fluorescence. Pulsed  $\text{N}_2$ -pumped or excimer pumped dye laser excitation of atomic species in acetylene flames, graphite furnaces, and inductively coupled plasmas have led to detection limits in the pg/mL range for many elements. The dye laser approach is unfortunately sufficiently complex and expensive to negate its general analytical use but is still useful for selected analyses where other analytical techniques are not satisfactory either due to poor detection power or more likely due to poor spectral selectivity.

Other analytical studies have included: evaluation of nebulizer-burner systems for atomic spectroscopy; analysis of trace elements in jet engine lubricating oils, in orange juice, in biological materials, and in environmental samples; development of a chemiluminescence method based upon  $\text{O}_3$  oxidation of metal hydrides and of a chemiluminescence method based upon metastable  $\text{N}_2$ - the  $\text{O}_3$  oxidation process is used to measure As, Bi, Sb, Te and Se and the metastable  $\text{N}_2$  excitation is used to measure polycyclic aromatic hydrocarbons in gases in gas chromatographic effluents; development of an inductively coupled plasma (ICP) source with either an ICP or a flame atomizer and atomic fluorescence detection

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